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Compositions and methods are provided for performing capillary electrophoresis using a composition comprising in combination in an aqueous buffered medium a coating polymer and a sieving polymer, where the sieving polymer is more hydrophilic than the coating polymer and is present in greater amount. Of particular interest are uncrosslinked acrylamide polymer mixtures for coating plastic channels and providing sieving for performing DNA separations in microfluidic devices. Polyacrylamide or N,N-dimethyl acrylamide is used with a N,N-dialkyl acrylamide copolymer, either separately or together for sieving and coating, serving as the medium in capillary electrophoresis DNA separations.